

CLAIMS

1. A method of enhancing the stability of a particulate suspension comprising an aqueous phase containing substantially no miscible organic solvent having suspended therein an agrochemical solid substantially insoluble in said aqueous phase which comprises

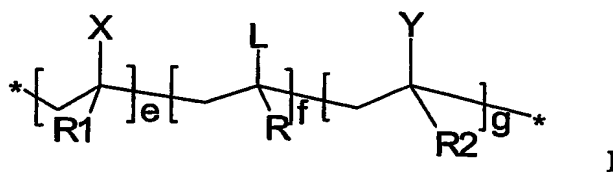
(i) forming a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety by polymerising a plurality of vinylic monomers, not being exclusively vinylic esters or their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking reactions and

(ii) reacting said polymeric stabiliser with one or more substances contained (dissolved or suspended) in the aqueous phase capable of undergoing a cross-linking reaction with said functional groups, wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended agrochemical is less than 1 part of polymeric stabiliser per 5 parts of suspended agrochemical.

2. A method according to claim 1 wherein the solid is milled or otherwise dispersed in the presence of the aqueous phase and the polymeric stabiliser prior to step (ii).

3. A method according to claim 1 or claim 2 wherein the particle size of the suspended agrochemical is from 1 to 10 microns.

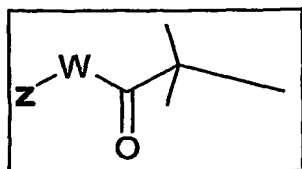
4. A method according to claim 1 wherein polymeric stabiliser is represented by the general formula (I):



wherein one \* represents the residue of an initiator group and the other \* represents the residue of a terminator group; R1, R and R2 are independently H or methyl; X is a hydrophilic moiety; L is a moiety containing a cross-linking group; Y is a hydrophobic moiety; the value of e is from 0 to 0.8; the value of f is from 0.05 to 0.4 and the value of g is from 0.10 to 0.90 and e + f + g equals 1, provided that when e is 0, \* represents the residue of a hydrophilic initiator.

5. A method according to claim 4 wherein the value of e is from 0.005 to 0.35, the value of f is from 0.01 to 0.4

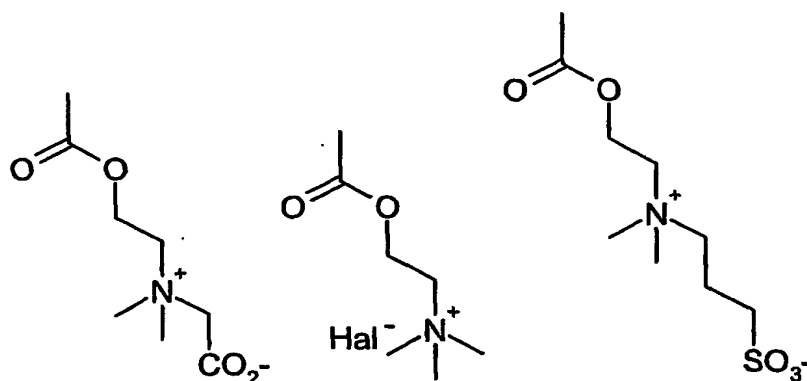
6. A method according to claim 4 or 5 wherein \* represents the residue of a hydrophilic initiator and said residue has the formula

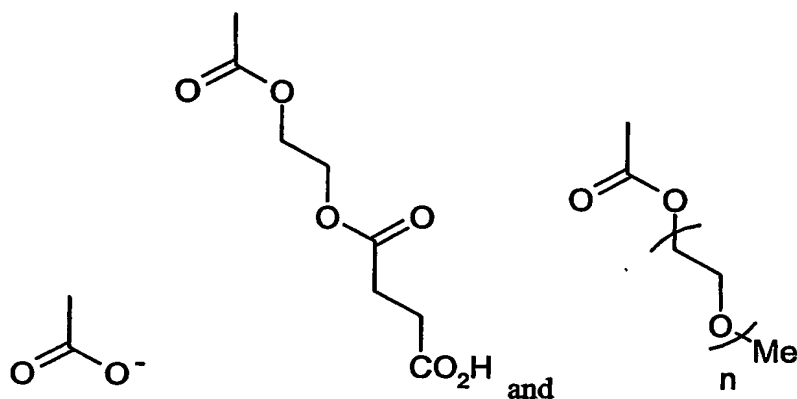


II

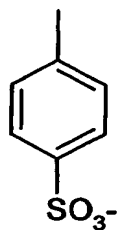
wherein Z is a hydrophilic group selected from C<sub>1</sub> to C<sub>4</sub> alkoxy polyethylene glycol, phenyloxy polyethylene glycol, poly(acrylamide), poly(vinyl pyrrolidone) or poly(methyl vinyl ether) and -W- is -O- or -NA- wherein A is hydrogen or C<sub>1</sub> to C<sub>4</sub> alkyl group.

7. A method according to any of claims 4 to 6 wherein the units E, F and G as herein defined correspond to one or monomers which is a methacrylate, an acrylate or a substituted styrene monomer.
8. A method according to claim 7 wherein -X is or carries a hydrophilic moiety X' selected from -SO<sub>3</sub><sup>-</sup>; polyethylene glycol optionally end-capped with C<sub>1</sub>-C<sub>4</sub> alkyl; -COOH or a salt thereof; carboxybetaine; sulfobetaine; and a quaternary ammonium salt -N<sup>+</sup>R<sup>3</sup><sub>3</sub>C<sup>-</sup> wherein each R<sup>3</sup> is independently H or C<sub>1</sub>-C<sub>4</sub> alkyl or -CH<sub>2</sub>CH<sub>2</sub>OH and wherein -L is or carries a cross-linking group L' selected from -OH; -SH; -NHA where A is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; and -COOH or a salt thereof and -Y is or carries a hydrophobic moiety Y' selected from -CO-O-(Si(CH<sub>3</sub>)<sub>2</sub>O)<sub>n</sub>-H wherein n is from 3 to 20; -CO-O-polypropylene glycol; -CO-O-A wherein A is a C<sub>1</sub>-C<sub>12</sub> alkyl group, cycloalkyl group, alkylcycloalkyl group, aralkyl group or alkylaryl group; and -CONHB wherein B is a C<sub>5</sub>-C<sub>12</sub> alkyl group.
9. A method according any of claims 4 to 8 wherein -X is selected from the groups



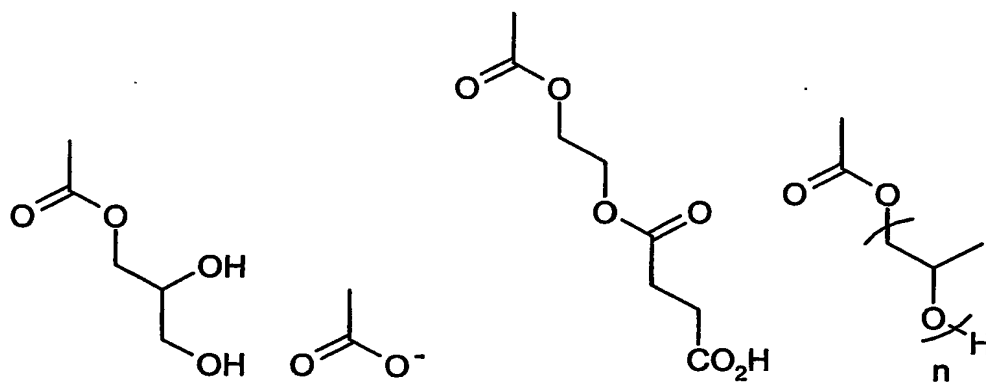
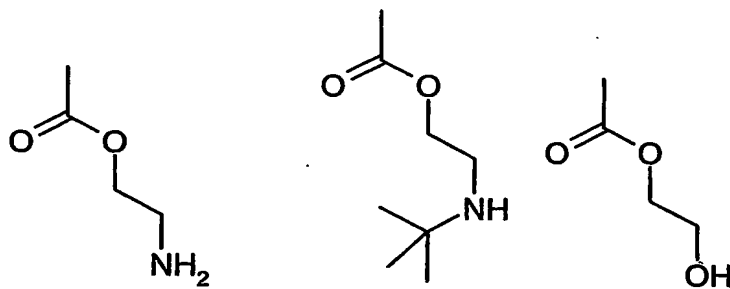


wherein  $n$  indicates the average degree of polymerisation of the polyethylene glycol chain and is from 5 to 100.



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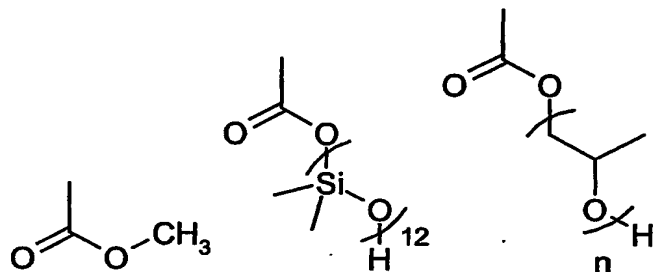
10. A method according any of claims 4 to 9 wherein  $-\text{L}$  is selected from the groups



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wherein  $n$  indicates the degree of polymerisation of the propylene glycol and is from 5 to 50

11. A method according to any of claims 4 to 10 wherein  $-Y$  is selected from the groups



wherein  $n$  indicates the degree of polymerisation of the propylene glycol and is from 5 to 50.

12. A method according to claim 1 wherein the polymeric stabiliser has a hydrophilic moiety, a hydrophobic moiety and a moiety that possesses reactive or cross-linking ability with respect to the one or more substances contained in the aqueous phase of the suspension and capable of undergoing a cross-linking reaction with said functional group and wherein the hydrophilic moiety is derived from one or more vinylic monomers selected from 2-(N,N-Dimethyl-N-(2-methacryloxyethyl) ammonium)ethanoic acid, 2-(trimethylammonium)ethyl methacrylate salt ; 3-(N,N-dimethyl-N-(2-methacryloxyethyl) ammonium)propyl-sulphonic acid, the sodium salt of methacrylic acid, mono-2-(methacryloxy)ethyl succinate, mono-methoxy poly(ethylene glycol) mono-methacrylate, styrene-4-sulfonic acid, 4-vinylbenzyl trimethyl ammonium chloride, 2-N-morpholinoethyl, 2-methacryloxyethylphosphonate methacrylate, 2-acrylamido-2-methylpropane sulphonic acid, mono-methoxy-PEO-(meth)acrylate, acrylamide, vinyl pyrrolidone, 2-sulphoethyl methacrylate, 2-acrylamido-2-methylpropane sulphonic acid, quaternary salts of dimethylaminoethyl methacrylate (DMAEMA) and of dimethylaminoethyl acrylate or DMAEMA at acid pHs, 2-(trimethylammonium)ethyl methacrylate iodide, 2-(N,N-dimethyl-N-(2-methacryloxyethyl) ammonium)ethanoic acid, or styrene-4-sulfonic acid and wherein the moiety that possesses reactive or cross-linking ability is derived from one or more vinylic monomers selected from

2-Aminoethyl methacrylate, 2-(tert-butylamino) ethyl methacrylate, 2-Hydroxyethyl methacrylate, 2,3-dihydroxypropyl methacrylate, the sodium salt of methacrylic acid, mono-2-(methacryloyloxy)ethyl succinate, poly(propylene glycol) mono-methacrylate, 2-aminoethyl methacrylate hydrochloride, N-(3-aminopropyl)methacrylamide hydrochloride, 4-aminostyrene, 2-(isopropylamino)ethylstyrene, 4-N-(vinylbenzyl)aminobutyric acid, 3-(N-styrylmethyl-2-aminoethylamino)-propyltrimethoxysilane hydrochloride, N-(3-methacryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane; 2-methoxy-4-vinylphenol, 4-vinylbenzyl alcohol, 4-vinylphenol, 2,6-dihydroxymethyl-4-methoxystyrene, 3,5-dimethoxy-4-hydroxystyrene, 2-hydroxy-3-methacryloxypropyl trimethyl ammonium chloride, 3-chloro-2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, diethylene glycol mono-methacrylate, 2-methacryloxyethyl glucoside, sorbitol methacrylate, caprolactone 2-methacryloxyethyl ester, 4-hydroxybutyl methacrylate, 2-hydroxypropyl methacrylate, acrylic acid, beta-carboxyethylacrylic acid, 4-vinylbenzoic acid, 4-((3-methacryloxy)propoxy)benzoic acid, mono-(2-(methacryloxy)ethyl)phthalate itaconic acid or iminated derivatives of these monomers once polymerised, glycidyl (meth)acrylate following conversion to reactive functional groups by reaction with alkylamines,

and wherein the hydrophobic moiety moiety is derived from one or more vinylic monomers selected from methyl methacrylate poly(dimethylsiloxane) mono-methacrylate, poly(propylene glycol) mono-methacrylate.

13. A method according to any of claims 4 to 12 wherein the polymeric stabilizer is a random graft or comb copolymer having a hydrophobic backbone and hydrophilic arms wherein R<sup>1</sup> is -H or methyl and -X is a group -CO-Z' where Z' is methoxy-(polyethylene glycol) having a degree of polymerisation (DP<sub>n</sub>) of 5-100 such that the moieties -CO-Z' form the hydrophilic "arms" of the random graft or comb copolymers and the remaining units form the hydrophobic backbone which also contains the cross-linking moieties L.

14. A method according to claim 13 wherein e is from 0.1 to 0.5, f is from 0.01 to 0.4 and g is from 0.1 to 0.9

15. A method according to any of claims 4 to 12 wherein the polymeric stabilizer is a block copolymer comprised of a hydrophilic block, which in turn is comprised of a hydrophile, which is a residue of the initiator of formula (II) as defined in claim 6 and/or a hydrophilic unit ( $-\text{CH}_2\text{CR}^1\text{X}-$ ) as defined in claim 4, said hydrophilic block being adjoined to a hydrophobic block which is comprised of randomly or sequentially copolymerised units ( $-\text{CH}_2\text{CR}_2\text{Y}-$ ) as defined in claim 4 and cross-linking units ( $-\text{CH}_2\text{CH}_2\text{CRL}-$ ) as defined in claim 4.

16. A method according to claim 15 wherein the value of  $f+g$  is from 0.2 to 1.0 and the ratio of  $g : f$  is from 1:2 to 1:10

17. A method according to any of the preceding claims wherein

(a) when the reactive functional group on the polymeric stabiliser is hydroxyl or thiol, the substance dissolved or suspended in the aqueous phase and capable of undergoing a cross-linking reaction with the said functional groups on the polymeric stabiliser suitable reaction partners is an isocyanate, an ester, an epoxide, a divinylsulphone or a glycerol triglycidyl ether or

(b) when the reactive functional group on the polymeric stabiliser is  $-\text{NHA}$  wherein A is hydrogen or a  $\text{C}_1$  to  $\text{C}_4$  alkyl group, the substance dissolved or suspended in the aqueous phase and capable of undergoing a cross-linking reaction with the said functional groups on the polymeric stabiliser is an isocyanate, an acetoacetoxy group, an aldehyde, an acrylate, a vinylsulphone, an epoxide, glycerol triglycidyl ether; glycerol propoxylate triglycidyl ether; trimethylolpropane triacrylate; trimethylolpropane propoxylate triacrylate; glutaric dialdehyde; 2-(acetoacetoxy) ethyl acrylate and 1,4-butanediol diacetoacetate or

(c) when the reactive functional group on the polymeric stabiliser is an acid reactive group, the substance dissolved or suspended in the aqueous phase and capable of undergoing a cross-linking reaction with the said functional groups on the polymeric stabiliser is an isocyanate, an aziridine or a carbodiimide.

18. A method according to claim 17 wherein the reactive functional group on the polymeric stabiliser is hydroxyl or thiol or  $-\text{NHA}$  and the substance dissolved or suspended in the aqueous phase and capable of undergoing a cross-linking reaction with the said functional groups on the polymeric stabiliser suitable reaction partners is an isocyanate wherein the isocyanate is selected from m-phenylene diisocyanate; 1-chloro-2,4-phenylene diisocyanate; 4,4'-methylenebis(phenyl isocyanate);

3,3'-dimethyl-4,4'-biphenylene diisocyanate 4,4'-methylenebis(2-methylphenyl isocyanate); 3,3'-dimethoxy-4,4'-biphenylene diisocyanate; 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate; tetramethyl-4,4'-biphenylene diisocyanate; isophorone diisocyanate; hexane-1,6-diisocyanate; tetramethylene xylene diisocyanate;  $\alpha$ ,4-tolylene diisocyanate; tolylene 2,5-diisocyanate; 2,4,6-trimethyl-1,3-phenylene diisocyanate; poly(ethylene adipate) tolylene 2,4-diisocyanate terminated; poly(isophorone diisocyanate); poly(propylene glycol) tolylene 2,4-diisocyanate terminated; poly(1,4-butanediol) tolylene diisocyanate terminated; 1,8-diisocyanatooctane; poly(hexamethylene diisocyanate); poly(tolylene 2,4-diisocyanate); poly(tetrafluoroethylene oxide-co-difluoromethylene oxide)  $\alpha$ , $\omega$ -diisocyanate; 1,4-diisocyanatobutane; 1,3-phenylene diisocyanate; 1,4-phenylene diisocyanate; trans-1,4-cyclohexylene diisocyanate; m-xylylene diisocyanate;  $\alpha$ , $\alpha$ -dimethyl- $\alpha$ ,4-phenylethyl diisocyanate; 4-bromo-6-methyl-1,3-phenylene diisocyanate; 4-chloro-6-methyl-1,3-phenylene diisocyanate; poly(1,4-butanediol) isophorone diisocyanate terminated; 3,3'-dimethyl-4,4'-biphenylene diisocyanate; and 1,3-bis(1-isocyanato-1-methylethyl)benzene.

20 A method according to any of claims 2 to 19 wherein the substance dissolved or suspended in the aqueous phase and capable of undergoing a cross-linking reaction is added to the aqueous phase after milling.

21 A method according to any of the preceding claims wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is from 1 part of polymeric stabiliser to 200 parts of suspended solid to 1 part of polymeric stabiliser per 10 parts of suspended solid.

22 A method according to any of the preceding claims wherein the polymeric stabiliser is prepared by atom transfer radical polymerisation.

23 A particulate suspension comprising a liquid phase having suspended therein a solid substantially insoluble in said liquid phase wherein the suspension is stabilised by the reaction product of

(i) a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety and comprising a plurality of vinylic monomers, not being exclusively of vinylic esters or

of their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking nucleophilic or condensation reactions and

(ii) one or more substances contained in the liquid phase capable of undergoing a cross-linking reaction with said functional groups

5 wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is less than 1 part of polymeric stabiliser per 5 parts of suspended solid by weight.